Investigations on the Chain Length Dependence of Radical Reactivity*

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The rate constant of the reaction scavenger S with radical R• in aqueous solutions has been determined as a function of the size of the radical. Scavengers were tetranitromethane (TNM) and *p*-nitrosodimethylaniline (PNDA). The radicals were produced by hydrogen atom abstraction from ethylene oxide oligomers and polymers. It was found that in both cases k_{R+S} is proportional to the diffusion coefficient of the radical R•, but it could be demonstrated that the reaction R• + PNDA is not encounter-controlled. The reaction R• + TNM is almost encounter-controlled. Its chain length independence at long chain length leads to the conclusion that the reaction is essentially determined by the diffusion of the scavenger and that the diffusion of the latter is not hindered within the coil of a macromolecule.

Kinetic treatments of macroradical reactions often contain the simplifying assumption that the radical reactivity is essentially independent of the chain length. A virtual independence of chain length is expected if the transport processes of the reactants are faster than the chemical reaction, *i.e.* in the case of activation-controlled reactions. However, in the case of diffusion-controlled reactions the rate constant will exhibit a complex dependence on radical size.

This problem has been the subject of several theoretical papers [1—7], since it is relevant to the diffusion-controlled termination step in the polymerization of vinyl compounds. The scarce experimental work on this topic has concerned mainly the combination of end group radicals of poly(methyl methacrylate) in various organic solvents [8, 9] and the combination of side group radicals of oligomers and polymers of ethylene oxide in aqueous solution [10]. The results seem to corroborate the concept of the segmental diffusion as the rate determining step in the interaction of macroradicals.

Whereas those investigations were concerned with the rate constant of the combination of radicals of equal size, the work reported here deals with the interaction of low-molecular--weight scavengers with radicals of various sizes. The scavengers *p*-nitrosodimethylaniline (PNDA) and tetranitromethane (TNM) were selected for their high reactivity towards low-molecular-weight radicals. Table 1 shows some values of the rate constant k_{R+S} at room temperature quoted from the literature. These values pertain to the order of encounter-controlled reactions. In the case of a small radical reacting with a scavenger the diffusion of both reactants is comparable. The rate constant therefore should be essentially

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Table 1

Bimolecular rate constants for the reactions of PNDA and TNM with substrate radicals at room temperature
(Radicals were produced from substrate molecules by hydrogen atom abstraction)

Source of radical	Scavenger	$k_{R+S} \times 10^{-9}$ $[M^{-1}\ s^{-1}]$	Ref.
CH_3OH	PNDA	0.79	[11]
CH_3CH_2OH	PNDA	2.42	[11]
$(CH_3)_2CHOH$	PNDA	3.22	[11]
sucrose	TNM	1.0	[12]
glucose	TNM	2.6	[12]
phenol	TNM	1.2	[12]
CH_3OH	TNM	5.0	[13]
$CH_3CH_2CH_2OH$	TNM	4.7	[13]
glycerol	TNM	2.4	[13]

determined by the diffusion coefficients of the radical D_R and the scavenger D_S. Since D_R decreases with increasing size of the radical the rate constant is expected to decrease. In the case of the reaction of a big macroradical with a scavenger molecule, the rate constant should depend mainly upon the diffusion of the scavenger. The influence of the size of the macroradical should be negligible as long as the diffusion of the scavenger molecule after penetration into the coil is not hindered by the polymer segments. In order to test the validity of these assumptions, the rate constants of the reaction of scavengers mentioned above with radicals of oligomers and polymers of ethylene oxide

$$S + -[-CH_2-\underset{\bullet}{C}H-O-]- \rightarrow \text{products} \qquad (1)$$

have been measured. The radicals were formed by the attack of OH• radicals according to

$$OH\bullet + -[-CH_2-CH_2-O-]- \rightarrow H_2O + -[-CH_2-\underset{\bullet}{C}H-O-]- \qquad (2)$$

OH• radicals were produced by irradiating aqueous solutions of the substrates with a short pulse (1 μsec) of 1.6 MeV electrons.

Experimental

Purification of reagents

The polyethylene oxide samples, obtained from Farbwerke Hoechst AG, were reprecipitated several times with diethyl ether from methanol solutions. Di- and triethylene glycol (puriss. grade) were supplied by Fluka AG and distilled before use.

All polymers were of low polydispersity, the ratio of weight to number average molecular weight being between 1.08 and 1.12. TNM (puriss. grade) supplied by Fluka was washed five times with distilled water. PNDA from Schuchardt GmbH was recrystallized three times from benzene. Triply distilled water was used for making up the solutions, which were deaerated by bubbling with N_2O. The gas was purified to remove oxygen beforehand by bubbling through Cr^{2+} solution and passing through a column filled with BTS catalyst from BASF.

Measurement of molecular weights

Weight average molecular weights were determined in methanol solution using a Sofica light scattering instrument. Number average molecular weights were determined in toluene solution using a vapour pressure osmometer (Knauer, Berlin) and a membrane osmometer (Mechrolab).

Determination of diffusion coefficients

Diaphragm diffusion cells similar to those described by *Holmes et al.* [14, 15] were used to measure the diffusion coefficients of TNM and PNDA in water at 25°C: $D_{TNM} = 1.075 \times 10^{-5}$ cm^2 s^{-1} and $D_{PNDA} = 6.86 \times 10^{-6}$ cm^2 s^{-1}. The cell constants were determined with 0.1 M-KI solution ($D_{KI} = 1.865 \times 10^{-5}$ cm^2 s^{-1} [16]). Concentrations were measured spectrophotometrically (KI: $\varepsilon_{226\,nm} = 1.4 \times 10^4\, M^{-1}$ cm^{-1}, PNDA: $\varepsilon_{440\,nm} = 3.42 \times 10^4\, M^{-1}$ cm^{-1}, TNM: $\varepsilon_{350\,nm} = 1.47 \times 10^4\, M^{-1}$ cm^{-1}, as nitroform anion after reduction with hydrazine sulfate).

All other diffusion coefficients are quoted from the literature [16—21].

Pulse radiolytic determination of the rate constant k_{R+S}

The solutions were irradiated with a 1 μsec pulse of 1.6 MeV electrons from a van de Graaff generator. The apparatus has been described elsewhere [22]. The solutions were saturated with N_2O thus converting all hydrated electrons into OH• radicals according to

$$e_{aq} + N_2O \xrightarrow{+H_2O} OH^- + OH\bullet + N_2. \qquad (3)$$

In order to choose appropriate reaction conditions it had to be considered that

a) practically all OH• radicals produced directly during the absorption of the fast electrons or *via* reaction (*3*) reacted with the dissolved ethylene oxide oligomers or polymers according to $OH\bullet + RH \rightarrow H_2O + R\bullet$,

b) the scavenger concentration was sufficiently high to ensure that nearly all radicals R• were scavenged according to reaction (*1*),

c) the combination R• + R• was essentially suppressed.

Taking into account considerations given elsewhere [11, 12], typical reaction conditions were: pulse dose *ca.* 100 rad corresponding to [OH] ≈ 6×10^{-7} mole l^{-1}, [RH] = 10^{-1} base mole l^{-1}, [S] = 1×10^{-5} mole l^{-1}.

In the case of the PNDA experiments the rate constant k_{R+PNDA} was determined by recording the change of the optical absorption at 440 nm with time. Since the consumption of PNDA was only *ca.* 5% of the initial [PNDA] the decrease in [PNDA] is expected to be first order. By designating the optical densities after time t and after a very long time after the pulse as E_t and E_∞ one obtains the expression

$$\log \frac{E_\infty - E_t}{E_\infty} = \frac{k_{R+S}\,[S]\,t}{2.303} \qquad (4)$$

The rate constant k_{R+PNDA} can be calculated from the slope of the straight line in a semilogarithmic plot of $(E_\infty - E_t)/E_\infty$ *vs.* time.

During the reaction TNM + R• one nitroform anion is produced for each radical scavenged. The determination of the rate constant k_{R+TNM} may be carried out therefore by recording the change of the optical absorption at 350 nm as a function of time and plotting $(E_\infty - E_t)/E_\infty$ *vs.* t in analogy to equation (*4*).

Results

Fig. 1 shows two examples of oscilloscope traces demonstrating the decrease in [PNDA] and the increase in $[C(NO_2)_3^-]$. Figs. 2 and 3 show plots according to equation (*4*) from typical runs with solutions containing polyethylene oxides of different chain length. The slope of the straight lines decreases with increasing degree of polymerization. The chain length dependence of the rate constant k_{R+S} is shown in Fig. 4. The points correspond to average values obtained from 5 to 8 independent determinations. In both cases k_{R+S} decreases relatively rapidly when the chain is short and approaches a limiting value at longer chain length. In order to determine the influence of diffusion on the rate constant, k_{R+S} was plotted in Fig. 5 as a function of the diffusion coefficient D_R of the various oligomers and polymers. In doing so, it was assumed that there is no appreciable difference between the diffusion coefficient of a substance RH and its radical R• produced by the abstraction of an hydrogen atom. The $D_{R\bullet}$ values (relative to pure water) were quoted from the literature [17—21] and pertain to $c \to 0$. Since D_R decreases with concentration these values do not correspond exactly to our reaction conditions. However,

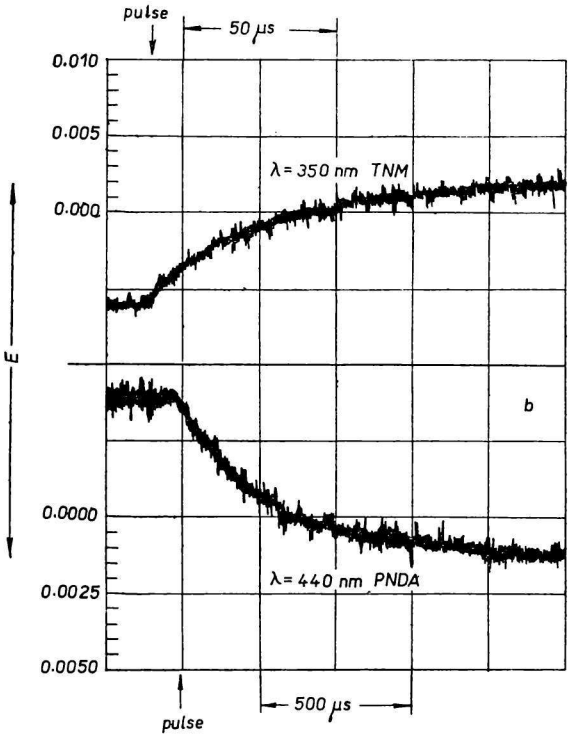

Fig. 1. Typical oscillograms obtained at 25°C with a polymer of $\overline{P}_n = 38$ demonstrating the increase and the decrease of optical densities due to the formation (curve *a*) of $C(NO_2)_3^-$ and the decay (curve *b*) in the concentration of PNDA.

a) [RH] = 10^{-1} base mole l^{-1}, [TNM] = 10^{-5} mole l^{-1}, pulse dose 100 rad; *b*) [RH] = = 10^{-1} base mole l^{-1}, [PNDA] = 10^{-5} mole l^{-1}, pulse dose 25 rad.

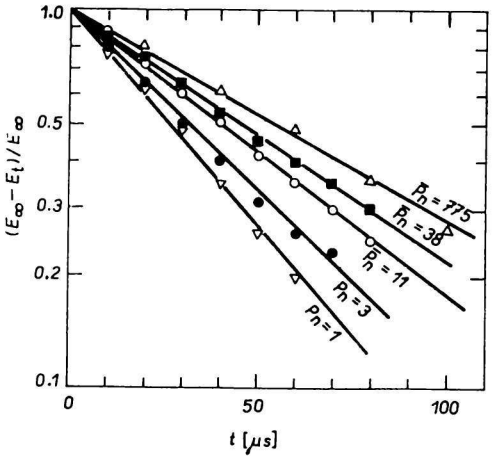

Fig. 2. The reaction TNM + R•. Plot according to equation (*4*). Pulse dose 100 rad, [TNM] = 9.5×10^{-6} mole l^{-1}, [RH] = 10^{-1} base mole l^{-1}.

measurements in the case of ethylene glycol [20] yielded $-(\Delta D/\Delta c) = 4.9 \times 10^{-7}$ $cm^2 s^{-1}$ $mole^{-1}$ l. The error therefore amounts to less than 1% in the concentration interval covered by our experiments. As can be seen from Fig. 5, for both scavengers the plot k_{R+S} *vs.* D_R yields a straight line leading to the formalism

$$k = \alpha + \beta D_R. \tag{5}$$

The temperature dependence of $k_{R\bullet+PNDA}$ was also determined for several oligomers and polymers. A typical Arrhenius plot is shown in Fig. 6. According to $k = A \exp(-E/RT)$ it was found $A \approx 8 \times 10^{10}$ $M^{-1} s^{-1}$ and $E = 3.0 \pm 0.5$ kcal $mole^{-1}$ independent of the radical size.

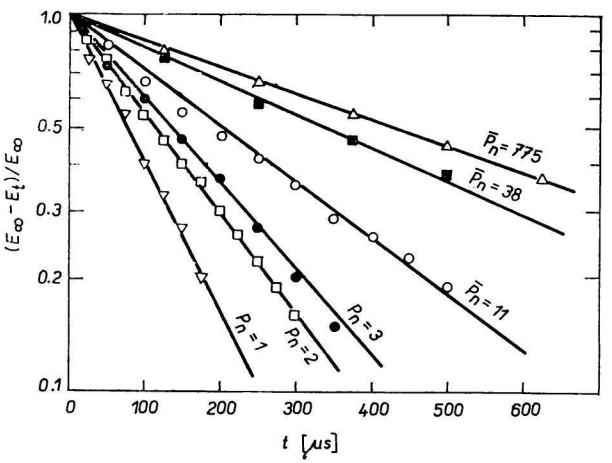

Fig. 3. The reaction PNDA + R•. Plot according to equation (*4*). Pulse dose 100 rad, [PNDA] = 9×10^{-6} mole l^{-1}, [RH] = 10^{-1} base mole l^{-1}.

Discussion

A relationship $k = f(D_R)$ as given by equation (5) may be expected from the application of the usual Smoluchowski treatment for encounter-controlled reactions to our data

$$k = 4\pi N_A\, 10^{-3}\, r(D_S + D_R). \tag{6}$$

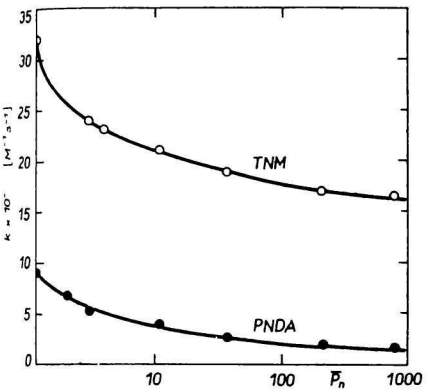

Fig. 4. The rate constant k_{R+S} as a function of chain length.

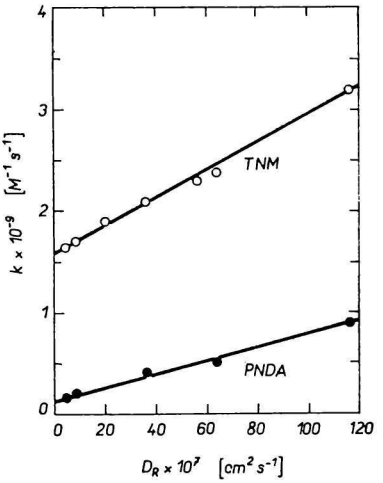

Fig. 5. The rate constant k_{R+S} as a function of the diffusion coefficient of the substrate.

Here N_A is the Avogadro number, D_S is the diffusion coefficient of the scavenger in [$cm^2 s^{-1}$], and r the reaction distance in [cm]. Since $\alpha = 4\pi N_A\, 10^{-3}\, r\, D_S$ and $\beta = 4\pi N_A\, 10^{-3}\, r$, D_S and r can be determined from the slope and the intercept of the straight

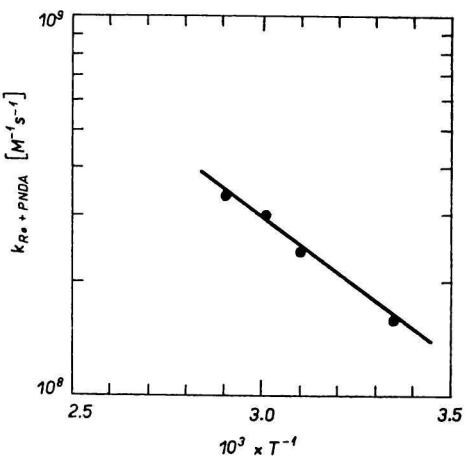

Fig. 6. Arrhenius plot of the rate constant k_{R+PNDA}; $\overline{P}_n = 775$.

line. The applicability of this tretament can be checked by comparing the experimental D_S (obtained from the diaphragm cell measurements) with that calculated.

Table 2 shows that in the case of TNM the two D_S values agree well. The reaction distance r is somewhat lower than the usually assumed value of 3 to 4 $\times$ 10^{-8} cm. Therefore the reaction of TNM with the radicals involved in this investigation may not be ideally encounter-controlled, *i. e.* the reaction probability per encounter may be somewhat less than unity.

Table 2

Comparison of diffusion coefficients of TNM and PNDA determined from kinetic data and by diaphragm cell measurements

Scavenger	D_S [cm^2 s^{-1}] from kinetic data equation (*6*)	D_S [cm^2 s^{-1}] from diaphragm cell measurements	r [cm]
TNM	1.15×10^{-5}	1.08×10^{-5}	1.64×10^{-8}
PNDA	1.8×10^{-6}	6.9×10^{-6}	0.9×10^{-8}

A much more pronounced deviation from encounter-controlled behaviour is found by applying the same treatment to the case of PNDA. The D_S from diaphragm cell measurements is about 4 times greater than that from the kinetic data, as shown in Table 2. Furthermore, the calculated r value of 0.9 $\times$ 10^{-8} cm is too small to be of relevance to reality.

One may conclude that investigations of the chain length dependence of radical reactivity allow a clearcut decision as to whether or not a reaction is encounter-controlled. In this connection it should be noted that the activation energies determined in the case of PNDA are relatively low and can be attributed to the activation energy of the diffusion process.

This reasoning implies two assumptions:

1. The reaction distance between the active centre of the macromolecule and the scavenger molecule is independent of the size of the radical.

2. The diffusion of a small particle is not hindered after penetration into the coil of a macromolecule.

This investigation cannot provide an argument against the first assumption. However, the validity of the second assumption is confirmed by the fact that the rate constant k_{R+S} approaches a limiting value with increasing chain length. If the diffusion within the coil would proceed with a slower rate than in the surrounding solvent one should expect steadily decreasing k_{R+S} values at high chain length. Thus, our results corroborate earlier findings of *Nishijima* and *Oster* [23] who performed diffusion measurements and fluorometric experiments with aqueous solutions of poly(vinylpyrrolidone). They found that the local viscosity for polymer concentrations less than 1% is nearly equal to the viscosity of the solvent although the macroscopic viscosity of the solution is significantly higher.

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